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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Process for the production of Shaped Articles from Polymer/Filler Compositions

We, DEUTSCHE GOLD-UND SILBER-SCHEIDEANSTALT vormals Roessler, of 9, Weissfrauenstrasse, Frankfurt (Main), Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the production of dimensionally and thermally stable elements or moulded bodies from polyolefine-filler mixtures, which contain organic peroxides as cross-linking agents. By polyolefines according to the invention, there are understood polymers which are formed from one or more olefines, and thus include copolymers and polymer mixtures.

The high frequency heating of electrically conducting materials has been known for a numbers of years. The material is in most cases heated by eddy current losses. This heating process is called inductive high-frequency heating.

Another process is used for heating material which is not electrically conducting. The non-conducting materials, for example synthetic plastic compositions, are traversed in the high frequency field by dielectric displacement currents and heated by the dielectric losses. This method of using high frequency heating is called a capacitative process. The general principles and conceptions concerning the theory of dielectric heating are described in a comprehensive article in the Journal "Kautschuk und Gummi" 11/1960, Year 13, page TW 355 *et seq.*

A preliminary condition for the capacitative high frequency heating of plastic compositions is a certain polarity of this material. If the molecular structure of the plastic compositions is not polar in character only very slight dielectric losses occur and a capacitative high frequency heating is not possible. Accordingly, elements consisting of insulation compositions, for example polyethylene, cannot be heated in this way.

It is also known that capacitative high frequency heating can be carried out by adding polar or electrically conducting substances to materials which by themselves cannot be heated dielectrically. Carbon black has, for example, been proposed as such a polar or electrically conducting substance.

Moreover, it has been proposed to place polymeric compositions, for example, of polyolefines, which contain carbon black, between two electrodes, to which is applied an electric potential with a frequency of at least 2 megacycles per sec. In this way, the filled material is quickly heated.

However, this process can only be carried out with certain types of carbon blacks, for example, those which have been produced by the so-called thermal process. If other types and quantities of carbon black are used, so that the plastic composition prepared with them comes into the electrically conductive range, the process is completely unsuitable. The reason for this is that at the instant at which the alternating field is applied to the electrodes, an electric discharges takes place through the filled plastic composition. The assembly being used cuts out immediately. The time which elapses between the application of the field and the discharge followed by the cut-out of the assembly amounts to a few fractions of a second only. This of course excludes any heating-up. If this sequence is repeated it is possible for the filled polymeric composition to ignite and begin to glow.

If an insulating material (paper or a laminated insulating material based on phenoplasts with paper as resin support, for example, that said under the Trade Mark "Pertinax" of Messrs. Dielektra, Porz on Rhine), is placed between the electrodes and a filled polymer, it is not possible in most cases to avoid a

[*Price 4s. 6d.*]

spark jump over the edge of the insulating material. It is therefore not possible to heat in this way conductive polymeric compositions.

It has moreover been known for a relatively long time that it is not possible to heat metallic materials in a manner analogous to the capacitative process in the microwave radiation field (for example frequencies of 2400 megacycles per sec. or a wavelength of 12.5 cm.), because the metallic materials reflect the electromagnetic waves.

It was all the more surprising to find that it is possible for polymeric compositions mixed with fillers having relatively good conductivity to be heated in the microwave radiation field. When using this process, the aforementioned difficulties are completely obviated. It is no longer necessary on account of the substantially higher frequency to work with specially shaped electrodes and spark discharges or other flash-overs no longer occur.

Accordingly, it is not necessary for carrying out the process of the invention to use electrodes which are adapted to the shape of the material to be cross-linked. In contrast hereto, it is essential in a number of cases that when using lower frequencies, for example 27 megacycles per sec., the shape of the electrode must be adapted to the external form of the workpiece and be brought as close as possible to the latter.

A process has now been found for the production of dimensionally and thermally stable elements from polyolefine-filler mixtures which contain one or more organic peroxides prior to the cross-linking and this process is characterised in that the polyolefine-filler mixtures made conductive by electricity-conducting fillers are shaped and brought into a high frequency alternating electrical field of at least 200 megacycles per sec. and are thereby cross-linked.

Accordingly the present invention provides a process for the production of dimensionally and thermally stable elements from polyolefine-filler mixtures containing an organic peroxide in amounts sufficient for cross-linking and effecting this by the heating of the starting mixture, during or after shaping of the structure, in a high-frequency, alternating electrical field, wherein the starting mixture contains a filler comprising carbon in an amount sufficient to produce suitable dielectric losses and that the cross-linking is effected by the action of a radiation field of a frequency of more than 200 megacycles per second.

The invention is based on the discovery that it is possible, with the aid of higher frequencies than used hitherto, to heat filled polyolefin compositions containing peroxide quickly and thereby carry out the cross-linking reaction at temperatures which are above the softening range of the polyolefine constituents without any deformation of the moulded elements occurring.

By the process according to the invention, synthetic plastic compositions which contain conductive fillers, for example, flame soot and graphite, and peroxides, can be quickly heated and cross-linked by this rapid heating. The advantages which are achieved by the cross-linking of, for example, polyethylene compositions containing carbon black, are known. In particular, due to the cross-linking, a better dimensional and thermal stability is produced by the cross-linking, and in certain cases with larger quantities of filler.

The process according to the invention is thus especially suitable for the heating and cross-linking of those compositions which have no dimensional stability under heat at the hardening or cross-linking temperature and thus lose the original shape on heating to temperatures of higher than about 125°C. The process is especially applicable to the cross-linking and hardening of tubes which, apart from the polymeric composition, the filler and the cross-linking agents, contain no other solidifying constituents.

In order to carry out the process of the invention, the composition, preferably containing at least 10 parts by weight of fillers and 0.5 part by weight of an organic peroxide to 100 parts by weight of polymer, is introduced into an electron furnace. This quantity of filler is necessary in order to produce the required dielectric losses, and the quantity of peroxide is necessary to obtain a certain cross-linking or hardening.

Under these conditions, however, a mixture which generally is still non-conductive is obtained when using a high-pressure polyethylene with an average molecular weight of about 40,000 and a filler. Depending on the nature of the filler used for loading purposes, different values of the electrical direct current resistance at room temperature are obtained with equal degree of loading. The following Table indicates these differences in connection with two carbon blacks obtained by different manufacturing methods:

Degree of loading	Specific direct current resistance at 22° C.	
	Flame soot	Thermal carbon black
10% by weight	$>10^{14}$	$>10^{14}$ Ω.cm
25% „ „	$>10^{14}$	$>10^{14}$ Ω.cm
33% „ „	2.10^{7}	$>10^{14}$ Ω.cm
50% „ „	8	1.10^{14} Ω.cm
70% „ „	about 3—5	7.10^{4} Ω.cm

It is clear from this Table that a flame soot with an average particle size of about 1150 Å is especially suitable for use in the process according to the invention. It is possible in principle for all carbon blacks to be used in accordance with the process provided that the quantity thereof in the polymer to be heated is sufficient in order to supply the necessary dielectric losses which are essential for the high frequency heating. Gas, acetylene and furnace soots are also suitable for this purpose, and as such or in admixture with one another.

The process of the invention is carried out in a particularly advantageous manner if the dielectric loss factor is brought to the order of magnitude of 1 or greater than 1 by adding a filler of a filler mixture. It is obvious that the dielectric constant of the polymeric mixture is changed in addition to the dielectric loss factor.

If the conductivity of a polyolefine-carbon black mixture is to be greatly increased without the proportion of filler being too high, it is advantageous to use carbon black-graphite mixtures. For this purpose, it is preferred to use powdered or flaked graphite. With this variant of the process, relatively high conductivities are produced with relatively low filler concentrations, such as cannot be achieved by using one component by itself.

The use of graphite by itself is not always recommended, since the mechanical properties of a graphite-polyolefine mixture are generally less satisfactory than those of a comparable polyolefine-carbon black mixture. The upper limit of the filler additive is determined by the mechanical properties resulting after cross-linking has taken place. If the polymeric composition is diluted to too great an extent by the addition of filler, there is no longer any sufficient contact between the individual polymer particles and the mechanical properties are greatly reduced. In this case the addition of filler is too high on account of the properties which it is desired to reduce. In practice, the upper limit to which the addition of filler can extend is reached with 250 parts by weight of filler to 100 parts by weight of polymer.

The high frequency heating can in principle also be carried out using quantities of filler smaller than 10 parts by weight and up to 100 parts by weight of polymer, but the operative times of the high frequency field are then usually so long that the advantages set forth above are cancelled out.

Suitable polymers for use with the process of the invention are polymerisation and copolymerisation products or polymerisation mixtures of ethylene, propylene and butylene, which constitute firm and plastic compositions at room temperature and which can be cross-linked with organic peroxides, despite their saturated chemical character.

Especially suitable peroxides for use in the process of the invention, are those organic peroxides which have at least one tertiary carbon atom in addition to the peroxide grouping. Such peroxides are di - tert. - butyl peroxide, dicumyl peroxide, cumenehydroperoxide and cumyl - tert. - butyl peroxide.

The following peroxides can also be used: di - α - phenylethyl peroxide, di - α - p - isopropylcumyl peroxide, di - α - nitro - cumyl peroxide, bis - 3,4 - dichloro - α - α - dimethylbenzyl peroxide, α - cumyl - α - p-tert. butylcumyl peroxide, α - cumyl - α - p-xylyl peroxide, α - cumyl - α - diphenylmethyl peroxide, α - cumyl - α,α^1-naphthylmethyl peroxide, α - cumyl - α - p-nitrocumyl peroxide and the like.

Hydroperoxides of suitable structure are advantageously used in admixture with a diperoxide. The upper limit of the peroxide content is not decisive and the cross-linking density is not to any appreciable extent dependent on the peroxide concentration.

In order to carry out the process of the invention, it is sometimes also desirable to add small quantities of basic additives, such as guanidines, lead salts or lead oxide, magnesium oxide or zinc oxide to the composition consisting of the filler and polyolefine

which is to be cross-linked. The addition of these substances serves either to produce a better workability or promotes a series of properties important in the subsequent use of the polymer after cross-linking has taken place. Since the amount of the additives in the majority of cases is between 0.1 and 5% by weight, calculated on the total composition, the initial conditions for a dielectric heating by means of high frequency effects is not changed by this addition.

One particularly preferred variant of the process consists in that the microwave heating is carried out in a closed or pressure-tight system under an elevated pressure of a few atmospheres. In this way, bubbles are prevented from forming in the polymeric composition, which bubbles are to be attributed to absorbed volatile constituents of the filler or to decomposition products of the organic peroxide. In practice, about 5 atmospheres is to be assumed as the upper limit of the superatmospheric pressure.

The invention is further illustrated by the following Example.

EXAMPLE.

By mixing 100 parts of a normal commercial high-pressure polyethylene (LUPOEN* H 2033 of BASF) with 100 parts of a flame soot (DUREX* of DEGUSSA*) having an average particle size of 1150 Å and 2 parts of a 95% technical dicumyl peroxide, a homogeneous mass was produced in a rubber mixer and, after cooling, this mass was comminuted and thereafter processed on an extrusion machine to form tubes with an external diameter of 32 mm. and a wall thickness of about 3 mm.

Tube sections about 25 cm. long taken from the material which has not cross-linked were introduced into an electron furnace at room temperature. The effective output in the cavity resonator was between 1.6 and 1.8 kW and the frequency was 2400 megacycles per second. After the microwave radiation field had been in operation for only 55 seconds, a temperature of about 130°C. was measured with an inserted pyrometer. After another operational period of 15 seconds, the temperature was found to have risen to about 145°C. Although no higher temperature could be detected, even with repeated experiments, solubility determination showed that the material was cross-linked.

When the same material was heated while shaping to form an experimental plate or sheet in a vulcanisation press in prior known manner, for 70 seconds at 130 or 145°C., no cross-linking or hardening occurred. From this it can be assumed that the temperature in the composition which was exposed to the high frequency radiation field was for a short period substantially higher than could be measured by the insertion pyrometer.

* The words "Lupolen", "Durex" and "Degussa" are Registered Trade Marks.

WHAT WE CLAIM IS:—

1. A process for the production of dimensionally and thermally stable elements from polyolefine-filler mixtures containing an organic peroxide in amounts sufficient for cross-linking, and effecting this cross-linking by the heating of the starting mixture, during or after shaping of the structure, in a high-frequency, alternating electrical field, wherein the starting mixture contains a filler comprising carbon in an amount sufficient to produce suitable dielectric losses and that the cross-linking is effected by the action of a radiation field of a frequency of more than 200 megacycles per second.

2. A process as claimed in claim 1, wherein gas, flame, acetylene and/or furnace soot are used as the electricity-conducting fillers.

3. A process as claimed in claim 1 wherein powdered or flaked graphite, alone or in admixture with carbon black, is used as electricity-conducting filler.

4. A process as claimed in any of claims 1 to 3, wherein the composition to be cross-linked contains from 10 to 250 parts by weight of filler to 100 parts by weight of polymer.

5. A process as claimed in any of claims 1 to 4, wherein symmetrical or unsymmetrical peroxides, hydroperoxides or mixtures thereof are used as peroxides.

6. A process as claimed in any of claims 1 to 5, wherein the composition to be cross-linked contains at least 0.5 part by weight of peroxide or peroxide mixtures to 100 parts by weight of polymer.

7. A process as claimed in any of claims 1 to 6, wherein the composition to be cross-linked contains from 0.1—5 per cent by weight, calculated on the total composition, of basically reacting additives in addition to polymers, filler and cross-linking agents.

8. A process as claimed in any of claims 1 to 7, wherein the high frequency heating is carried out in a closed system under a superatmospheric pressure up to 5 atmospheres.

9. A process for the production of dimensionally and thermally stable shaped structures substantially as described with reference to the Example.

10. Dimensionally and thermally stable shaped structures produced by the process claimed in any of the preceding claims.

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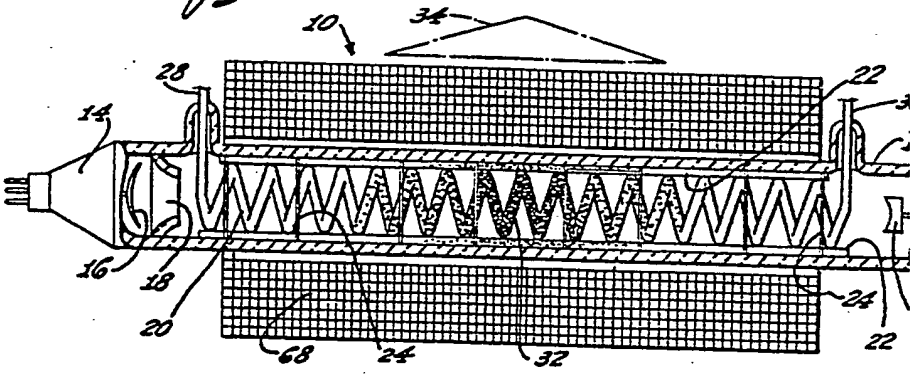
Fig. 2

Fig. 1



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Sheet 1

Fig. 2

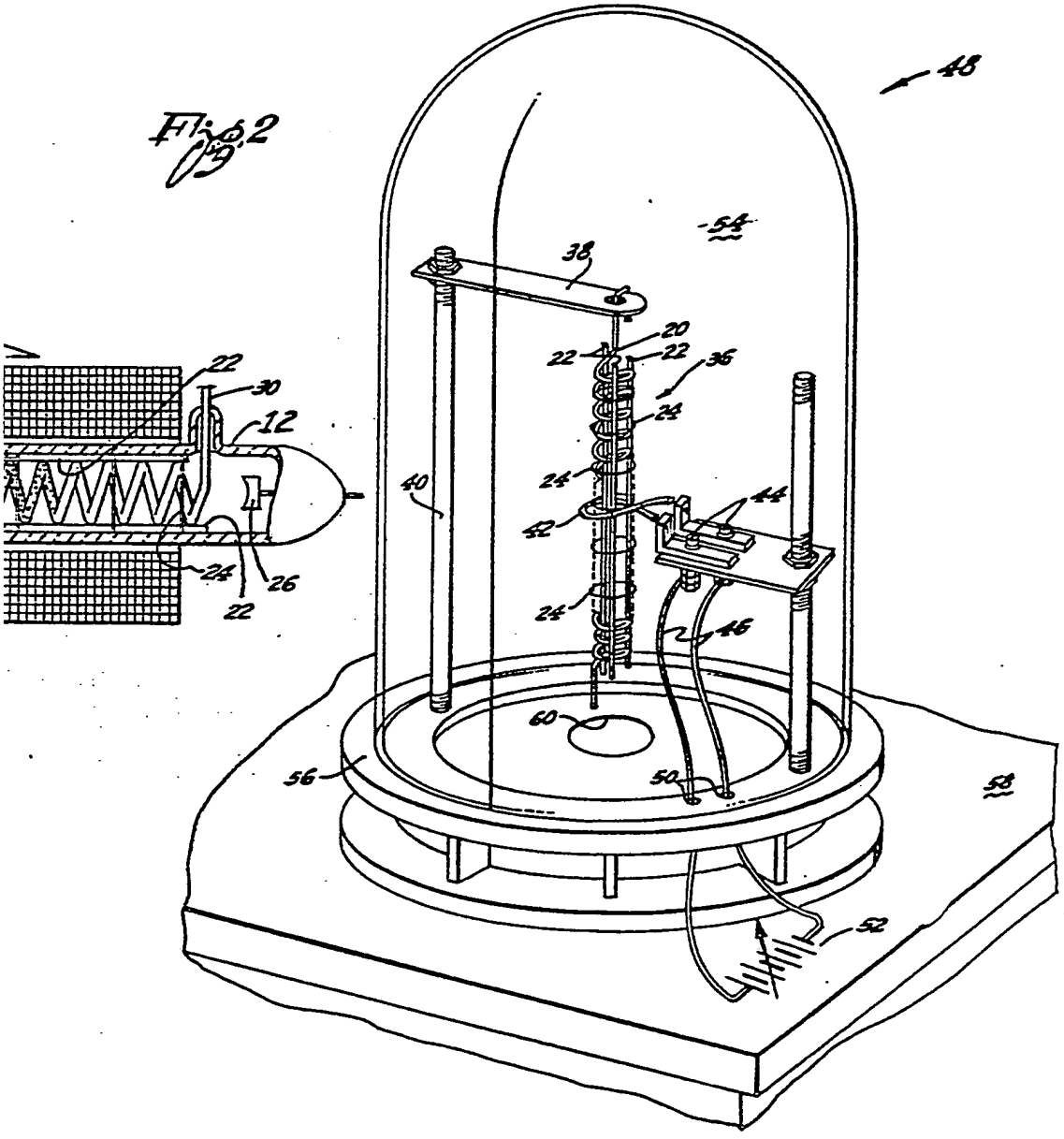
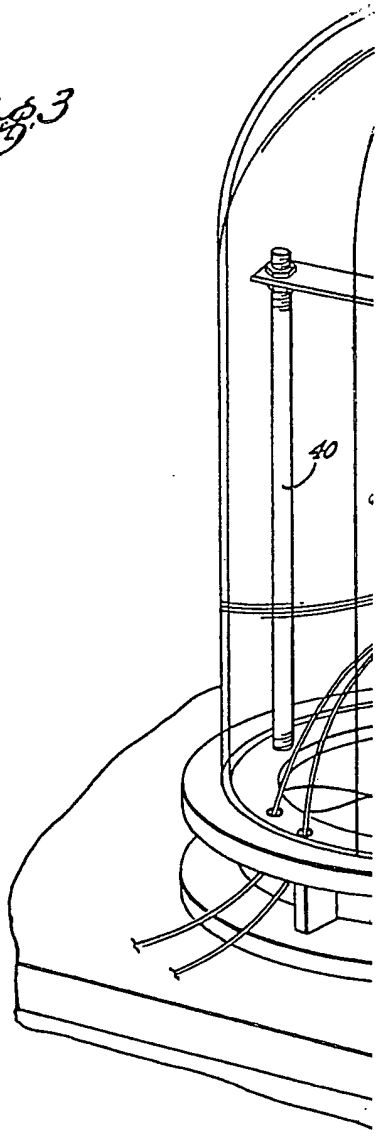


Fig. 3



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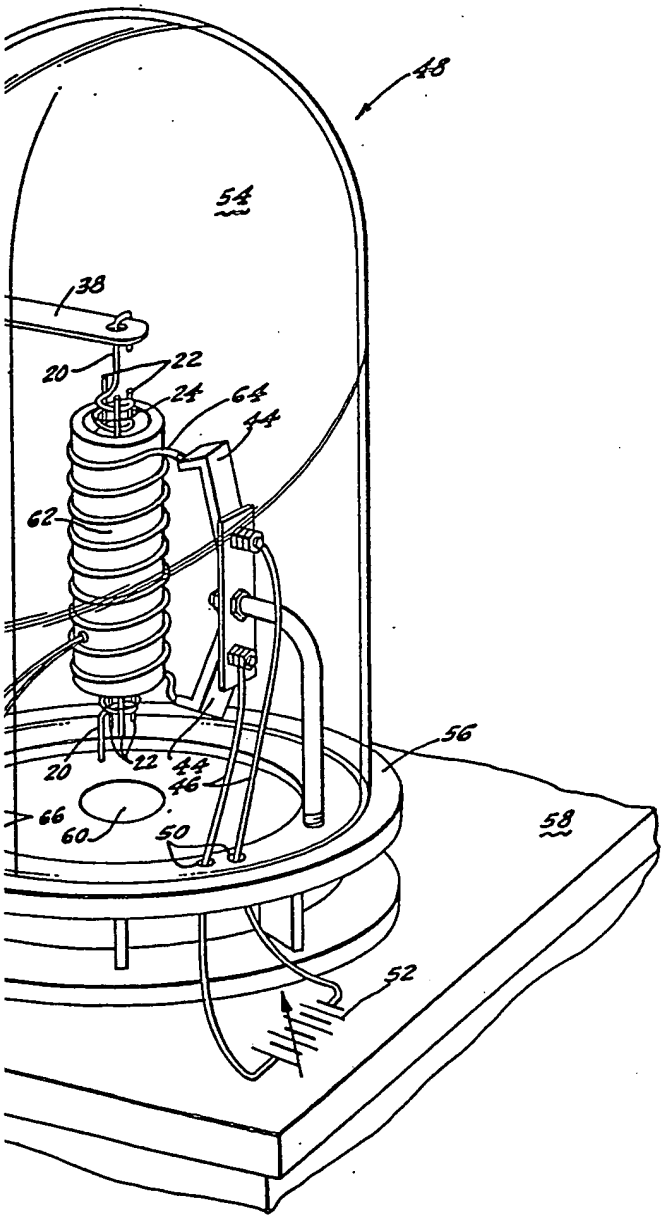

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Sheet 2

Fig. 3